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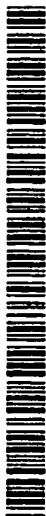


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(54) Title: PLASTICIZED POLYPROPYLENE THERMOPLASTICS

(57) Abstract: The invention is directed to a plasticized polypropylene thermoplastic composition comprising a blend of A) from 50 to 99.9 wt % of a thermoplastic polymer derived from polypropylene, optionally with one or more copolymerizable monomer selected from C<sub>2</sub>-C<sub>10</sub> α-olefin or diolefin, said polymer having a melt flow rate (MFR) (ASTM D1238) of from 0.5 to 1000 and a crystallinity by differential scanning calorimetry of from 0 to 70 %; B) from 0.1 to 50 wt % of at least one ethylene copolymer having a weight-average molecular weight (M<sub>w</sub>) (GPC) of from 500 to 10,000, a molecular weight distribution (MWD) (GPC) of from greater than 1.5 to less than or equal to 3.5, and a comonomer content of from greater than or equal to 20 mol % to less than 70 mol %; and optionally, C) from 0 to 20 wt % of a thermoplastic polypropylene modifier compound other than that of B).

## PLASTICIZED POLYPROPYLENE THERMOPLASTICS

### FIELD OF INVENTION

5 This invention relates to hydrocarbon plasticizers for polypropylene thermoplastics.

### BACKGROUND

10 The blending of plasticizers in general with thermoplastics and the resulting plasticization of those thermoplastics are well known and many reviews have been written. A plasticizer is generally an organic compound incorporated into a high polymer, such as for example a thermoplastic, to desirably facilitate processing, increase its workability, flexibility, and/or distensibility of the polymer.

15 Within the last few years efforts have been made in the field of plasticizers to better understand factors which govern plasticizer/thermoplastic miscibility. Examples of a thermoplastic and plasticizer include polypropylene and low molecular weight polyolefins, respectively. Polypropylene is an inexpensive polyolefin engineering thermoplastic that is generally stiff and even brittle below room temperature especially for highly stereoregular polypropylene. Tackifiers  
20 are examples of low molecular weight polyolefins plasticizers. Examples of tackifiers include hydrocarbon resins derived from fractionated petroleum distillates, coal tar, turpentine fractions and from copolymerization of pure aromatic monomers. However, these tackifiers typically have high glass transition temperature ( $T_g$ ) and high solubility parameter. As such, upon blending, these  
25 tackifiers tend to raise the  $T_g$  of the polypropylene. Increasing the  $T_g$  increases the stiffness of polypropylene.

Other plasticizers, which have low  $T_g$  (below  $-20^{\circ}\text{C}$ ) such as ethylene-propylene rubber, ethylene-butene copolymer (having a  $M_w$  greater than or equal to 20,000), are immiscible with the polypropylene. Plasticizers which are  
30 immiscible with polypropylene tend to collect on the surface of the manufactured article, hinder the manufacturing process of articles made therefrom and may cause the resulting product to have generally undesirable features.

Because polypropylene is an inexpensive thermoplastic, there exists a need to improve its workability and to overcome its inherent stiffness and brittleness which limit its commercial application. Therefore, a need exist to safely and economically improve the workability, flexibility, and/or distensibility of polypropylene.

### SUMMARY OF THE INVENTION

Miscible blends of polypropylene with low molecular weight ethylene  $\alpha$ -olefin copolymer plasticizers have been discovered. By blending such miscible, low molecular weight ethylene  $\alpha$ -olefin copolymer plasticizers with polypropylene (isotactic polypropylene, syndiotactic polypropylene and atactic polypropylene), the glass transition temperature, storage modulus and viscosity of the blended polypropylene are lowered. By decreasing the transition temperature, storage modulus and viscosity, the workability, flexibility, and distensibility of polypropylene improves. As such, broadened commercial application for these new polypropylene blends in film, fibers and molded products is apparent. Furthermore, the flexibility of a product design utilizing these novel blends can be further extended by taking advantage of the enhanced comonomer incorporation and tacticity control possible with metallocene catalysts, both of which can reduce isotactic polypropylene ("iPP") crystallinity prior to blending with the low molecular weight ethylene  $\alpha$ -olefin copolymer plasticizers.

In one embodiment, a plasticized polypropylene thermoplastic is provided. The plasticized polypropylene thermoplastic includes from 50 to 99.9 weight percent ("wt%") of a thermoplastic polymer derived from polypropylene. Optionally, the thermoplastic polymer is copolymerizable with one or more monomers selected from  $C_2$ - $C_{10}$   $\alpha$ -olefin or diolefin. The thermoplastic polymer desirably has a melt flow rate (MFR) (ASTM D1238) in the range of from 0.3 to 1000 and a crystallinity, determined by differential scanning calorimetry (DSC) at a scan rate of  $10^\circ\text{C}$  per minute, in the range of from 0 to 70% crystallinity. The thermoplastic polymer is blended with from 0.1 to 50 wt % of at least one ethylene copolymer. The ethylene copolymer desirably has a weight-average molecular weight ( $M_w$ ) (GPC) of from 500 to 10,000, a molecular weight

distribution (MWD) (GPC) of from greater than 1.5 to less than or equal to 3.5, and a comonomer content of from greater than or equal to 20 mol% to less than 70 mol%. The plasticized polypropylene thermoplastic may include from 0 to 20 wt% of the polypropylene thermoplastic composition, of a thermoplastic polypropylene modifier compound other than the ethylene copolymer described above. Examples of thermoplastic polypropylene modifier compounds include one or more compositions selected from the group which includes antioxidants, fillers, pigments, hydrocarbon resins, rosins or rosin esters, waxes, UV stabilizers, additional plasticizers, and tackifiers such as ESCOREZ, a product of Exxon Chemical, which is more fully described in U.S. Patent 5,317,070 which is incorporated by reference herein. Additionally, the terminal vinylidene groups present on some of the above thermoplastic polypropylene modifier compounds may be functionalized, such functionalization being more fully described in U.S. Patents 5,763,556 and 5,498,809, both of which are incorporated by reference herein.

The ethylene copolymer may be further described as having a glass transition temperature ( $T_g$ ) of from greater than or equal to  $-80^{\circ}\text{C}$  to less than or equal to  $-30^{\circ}\text{C}$ . In another embodiment, the ethylene copolymer may be described as having an ethylene crystallinity, as determined by differential scanning calorimetry (DSC) at a scan rate of  $10^{\circ}\text{C}$  per minute of less than or equal to 5% crystallinity.

In another embodiment, the plasticized polypropylene thermoplastic may be further described as having a crystallinity by DSC at a scan rate of  $10^{\circ}\text{C}$  per minute of less than 60 % and wherein the wt% of said ethylene copolymer present in the plasticized polypropylene thermoplastic is less than or equal to y, wherein y is in the range of 0.1 to 50, as determined by y in the equation

$$y = 50 - 0.5x$$

where x = the % crystallinity of the thermoplastic polymer.

In another embodiment, the thermoplastic polymer may be further described as having a crystallinity by DSC at a scan rate of  $10^{\circ}\text{C}$  per minute of greater than or equal to 60 % and wherein the wt % of said ethylene copolymer present in the plasticized polypropylene thermoplastic can be as high as 20.

In another embodiment, the ethylene copolymer component may include, in addition to ethylene, one or more of C<sub>3</sub> to C<sub>20</sub> linear or branched  $\alpha$ -olefin or diolefin. Desirably, the ethylene copolymer may be either an ethylene-propylene, ethylene-butene copolymer, ethylene-hexene copolymer, ethylene-octene copolymer, ethylene norbornene, ethylene styrene copolymers, and ethylene-isobutylene copolymers or mixed monomers including ter-, tetrapolymers, and the like, thereof.

In another embodiment, a plasticized polypropylene thermoplastic composition is provided which includes a blend of a thermoplastic polymer and the ethylene copolymer. The thermoplastic polymer is desirably derived from amorphous propylene. Desirably, from 50 to 99.9 wt% of the plasticized polypropylene thermoplastic is the thermoplastic polymer. Optionally the thermoplastic polymer may include one or more copolymerizable monomers selected from C<sub>2</sub>-C<sub>10</sub>  $\alpha$ -olefin or diolefin. The thermoplastic polymer has melt flow rate (MFR) (ASTM D1238) in a range from 0.3 to 1000 and a crystallinity, as determined by differential scanning calorimetry (DSC at a scan rate of 10 °C per minute), in a range from 0 to less than 5%. Desirably, from 0.1 to 50 wt % of the plasticized polypropylene thermoplastic is the ethylene copolymer. The ethylene copolymer has a weight-average molecular weight (M<sub>w</sub>) (GPC) in a range from 500 to 10,000, a molecular weight distribution (MWD) (GPC) in a range from greater than 1.5 to less than or equal to 3.5, and a comonomer content in a range from greater than or equal to 20 mol% to less than 70 mol%. The plasticized polypropylene thermoplastic may also include from 0 to 20 wt % thereof of a thermoplastic polypropylene modifier compound other than the ethylene copolymer. Examples of this thermoplastic polypropylene modifier include, but are not limited to, antioxidants, fillers, pigments, hydrocarbon resins, rosins or rosin esters, waxes, UV stabilizers, additional plasticizers, singularly or in combination.

In another embodiment, the plasticized polypropylene thermoplastic may be further described as having a crystallinity by DSC at a scan rate of 10 °C per minute of less than 5 % and wherein the wt% of said ethylene copolymer present

in the plasticized polypropylene thermoplastic is less than or equal to y, wherein y is in the range of 0.1 to 50, as determined by y in the equation

$$y = 50 - 0.5x$$

where x = the % crystallinity of the thermoplastic polymer.

5 In another embodiment, a plasticized polypropylene thermoplastic composition is provided which includes a blend of a thermoplastic polymer and the ethylene copolymer wherein the wt% of the ethylene copolymer in the plasticized polypropylene thermoplastic is less than or equal to y, wherein y is in the range of 0.1 to 50, as determined by y in the equation

10 
$$y = 50 - 0.5x$$

where x = the % crystallinity of said thermoplastic polymer. The thermoplastic polymer is derived from polypropylene, optionally with one or more copolymerizable monomer selected from C<sub>2</sub>-C<sub>10</sub> α-olefin or diolefin, said thermoplastic polymer having a melt flow rate (MFR) (ASTM D1238) of from 0.3 to 1000. The ethylene copolymer has a weight-average molecular weight (M<sub>w</sub>) (GPC) of from 500 to 10,000, a molecular weight distribution (MWD) (GPC) of from greater than 1.5 to less than or equal to 3.5, and a comonomer content of from greater than or equal to 20 mol % to less than 70 mol %. In one embodiment, from 50 to 99.9 wt % of the plasticized polypropylene thermoplastic is derived from the thermoplastic polymer and from 0.1 to 50 wt % of the plasticized polypropylene thermoplastic is derived from the ethylene copolymer. Desirably, the crystallinity, by differential scanning calorimetry (DSC at a scan rate of 10°C per minute), of the thermoplastic polymer is in a range of from 0 to 70%.

25 In another embodiment, a plasticized polypropylene thermoplastic composition formed from a blend of a thermoplastic polymer and an ethylene copolymer is provided. The thermoplastic polymer derived from polypropylene, optionally with one or more copolymerizable monomer selected from C<sub>2</sub>-C<sub>10</sub> α-olefin or diolefin, said thermoplastic polymer having a melt flow rate (MFR) (ASTM D1238) of from 0.3 to 1000. The ethylene copolymer has a weight-average molecular weight (M<sub>w</sub>) (GPC) of from 500 to 10,000, a molecular weight distribution (MWD) (GPC) of from greater than 1.5 to less than or equal to 3.5,

30

and a comonomer content of from greater than or equal to 20 mol % to less than 70 mol %. The wt % of the ethylene copolymer in the thermoplastic composition is less than or equal to y, wherein y is in the range of 0.1 to 50, as determined by y in the equation

5 
$$y = 50 - 0.5x$$

where x = the % crystallinity of said thermoplastic polymer.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 illustrates the relationship between the wt% copolymer present in the plasticized polypropylene thermoplastic and % crystallinity of the plasticized polypropylene thermoplastic.

Figure 2 illustrates dynamic mechanical thermal analysis measurements of a 50:50 blend of atactic polypropylene and Copolymer 1 (an ethylene-butene copolymer, see Table 1).

Figure 3 illustrates a tan  $\delta$  peak for the blend in Figure 2.

Figure 4 illustrates NMR relaxation measurements ( $T_{1\rho H}$ ) for a blend of atactic polypropylene and Copolymer 2 (an ethylene-butene copolymer, see Table 1).

Figure 5 illustrates the decreasing effect on Young's modulus of isotactic polypropylene by blending Copolymers 1-3 therewith (Copolymer 3 is an ethylene-butene copolymer, see Table 1).

Figure 6 illustrates that energy-to-break for the tensile bars increases over 50% due to addition of ~5-15 wt% plasticizer.

Figure 7 illustrates a hysteresis series of tensile curves for 60:40 wt:wt blend of elastomeric polypropylene and Copolymer 2.

#### **DETAILED DESCRIPTION OF THE INVENTION**

This invention relates to (1) plasticized polypropylene thermoplastic compositions, particularly miscible blends of polypropylene with low molecular weight ethylene  $\alpha$ -olefin copolymer plasticizers; (2) methods for making plasticized polypropylene thermoplastic compositions; and (3) products made from plasticized polypropylene thermoplastic compositions. These are described in turn below.

As used herein, "isotactic" is defined as having at least 95% isotactic (meso) pentads according to analysis by  $^{13}\text{C}$ -NMR. As used herein, "highly isotactic" is defined as having at least 99% isotactic pentads according to analysis by  $^{13}\text{C}$ -NMR.

5 As used herein, "amorphous" is defined as having less than 5% crystallinity as measured by DSC at a scan rate of 10 °C per minute.

As used herein, "molecular weight" means weight average molecular weight ( $M_w$ ) and "molecular weight distribution," (MWD), means  $M_w$  divided by number average molecular weight ( $M_n$ ) as determined by gel permeation chromatography (GPC). As used herein, unless otherwise stated, "polymerization" means homopolymerization.

10 The plasticized polypropylene thermoplastics described herein are a blend of a thermoplastic polymer and an ethylene copolymer. This blend may also include thermoplastic polypropylene modifiers. These modifiers may be included in the plasticized polypropylene thermoplastic compositions. Such modifiers (also known as additives) and their use are generally well known in the art.

#### Ethylene Copolymer Compositions

Generally, ethylene copolymers suitable for blending with the thermoplastic polymer, including amorphous and isotactic thermoplastic polymers, desirably have a weight-average molecular weight ( $M_w$ ) (GPC) of from 500 to 10,000, a molecular weight distribution (MWD) (GPC) of from greater than 1.5 to less than or equal to 3.5, and a comonomer content of from greater than or equal to 20 mol % to less than 70 mol %. The wt % of at least one ethylene copolymer present in the plasticized polypropylene thermoplastic composition may be from 0.1 to 20 wt%, desirably from 1.0 to 15 wt% and more desirably from 1.0 to 10 wt%. Specific examples of ethylene copolymers include, but are not limited to ethylene-propylene, ethylene-butene, ethylene-hexene, and ethylene-octene copolymers. Additionally, the ethylene copolymer desirably has a glass transition temperature ( $T_g$ ) in the range from greater than or equal to -80 °C to less than or equal to -30 °C, more desirably from -75 °C to -45 °C, most desirably, from -70 °C to -45 °C.



Table 1 illustrates the glass transition temperatures, measured by DSC at a scan rate of 10°C per minute, molecular weights and comonomer concentration of three ethylene/butene copolymers.

DSC was measured on a TA Instruments model number 2910. Generally, DSC is a measure of the heat flow into or away from a sample polymer. The sample polymer is placed in one heating chamber, a reference material into a separate heating chamber. The sample and a reference material are heated at a predetermined rate until heat is emitted or consumed by the sample. The DSC circuitry is programmed to maintain the same temperature for both the reference and sample chambers. The current necessary to maintain a constant temperature between the sample and reference is recorded. This data provide a direct measure of the heat of transition of the sample.

Table 1.

Ethylene Copolymer (Liquid)	Mole % comonomer (butene)	M <sub>w</sub> , GPC (PE std)	T <sub>g</sub> (DSC, °C)
Copolymer 1	33.3	7550	-71 (-45) <sup>a</sup>
Copolymer 2	60	8780	-55.3
Copolymer 3	66.7	6550	-61.2

<sup>a</sup> Small second transition in DSC.

Table 1A illustrates the molecular weights and comonomer concentration of two ethylene/propylene copolymers.

Table 1A.

Ethylene Copolymer (Liquid)	Mole % comonomer (propylene)	M <sub>w</sub> , GPC (PE std)	T <sub>g</sub> (DSC, °C)
Copolymer 4	38	21,900	Not Measured
Copolymer 5	42	3400	-76.0(-52) <sup>a</sup>

<sup>a</sup> Small second transition in DSC.

Copolymers 1-5 may be made in a high pressure reactor. An example of such a high pressure reactor would be a staged and baffled reactor (5 zones) and have a reactor volume 750 liters, and a 6:1 length/diameter dimension. The residence time in such a reactor may be between 1-2 minutes.

More particularly, the polymerization conditions for copolymers 1-5 would include a stirred 750 liter steel autoclave reaction vessel which is equipped to perform continuous Ziegler-Natta (Z-N), metallocene or other single site catalyst polymerization reactions at pressures up to 2500 bar and temperature up to 300°C. The reactor system may be equipped with instrumentation, such as thermocouples and pressure transducers to continuously monitor temperature and pressure and continuous feed systems to continuously supply purified compressed monomers (e.g., ethylene, butene-1). Additional equipment may also include a continuous catalyst feed system, a rapid venting and quenching system, and a product separation and collection system. The polymerization may be performed without the addition of any external solvents. The reactor contents may be stirred continuously during polymerization. A typical stirring rate may be about 2,000 rpm. The temperature in the reactor may be established and maintained at a target level, such as between 100°C and 220°C by pumping the catalyst solution using a continuous high pressure injection pump. See for example, US patents 5,084,534 and 5,408,017 incorporated by reference for purposes of US patent practice.

Following polymerization, the polymerized product may be separated and analyzed, for such purposes as quality control and the like. The unreacted ingredients may be transported via a recycle loop through a cooler and compressor and returned back to the autoclave reactor, along with fresh monomer. As will be recognized by those skilled in the art of high pressure Z-N polymerization, the process allows considerable flexibility to modify the molecular weights and copolymer composition, among other parameters of the polymerized products.

More specific reactor conditions may include the use of  $\text{Me}_2\text{Si}(\text{H}_4\text{-Indenyl})_2 \text{ZrCl}_2$  as the catalyst and methyl alumoxane (MAO) as the co-catalyst. The Al/transition metal molar ratio may range from 50:1 to 500:1. Reactor pressure may be 20,000 psi or approximately 1350 bar. The reactor exit temperature may be in the range of between 300°F to 370°F, depending upon the target molecular weight. The composition feed may be 90 mole % butene-1 and 10 mole % ethylene to achieve a target 50 wt. % incorporation of butene-1 into the ethylene copolymer. Under these conditions, a production rate of around 2750 lbs/hr. may be achieved.

The viscosity measurements for copolymers 1, 3-5 are provided in Table 2. In keeping with the GPC molecular weight measurements, the viscosity of Copolymer 1 is higher than that of Copolymer 2. These viscosities were measured using a Brookfield Viscometer.

Table 2.

## Viscosity

Liquid	Viscosity (cP @ °C)			
	50	60	70	90
Copolymer 5	1255	715	485	
	1200	695	445	200
Copolymer 1	50	70	90	110
	8810	2850	1230	
		2910	1250	580
Copolymer 3	6010	1880	730	
		1840	750	360
Copolymer 4	110	120	140	
	54,500	39,800	22,800	

The wt % of the ethylene copolymer present in the plasticized polypropylene thermoplastic may be described by Equation 1, wherein the wt % of the copolymer is less than or equal to y, wherein y is in the range of 0.1 to 50, as determined by y in Equation 1:

$$y = 50 - 0.5x$$

where x = the % crystallinity of the thermoplastic polymer composition (described in greater detail below). The relationship between wt % copolymer present in the plasticized polypropylene thermoplastic and % crystallinity is further illustrated in Figure 1.

#### Thermoplastic Polymer Compositions

Generally, thermoplastic polymers suitable for use in this invention may be derived from propylene or may be copolymerized with small amounts, generally from 0.1 to 10 mol. % of one or more monomers selected from C<sub>2</sub>-C<sub>10</sub> α-olefins or diolefins such as for example, ethylene, butene-1, hexene-1 and octene-1. These thermoplastic polymers include copolymers and homopolymers